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NEW PIGMENTS FOR TINTING VITREOUS COATINGS ON CERAMICS

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New ceramic pigments that have been obtained using nontraditional materials, namely chicken and ostrich eggshell, are considered.

The information on glazes and ceramic pigments is extensive and diverse. It considers in detail nearly all issues related to the chemistry and production technology of these materials [1 – 6].

It is usually recommended to introduce oxide forms of different elements into an initial pigment mixture. These elements interact under thermal treatment and produce composites of a particular mineralogical composition. When natural compounds of such oxides are used, they cannot ensure pure tinting upon introducing the obtained pigments into glazes. Therefore, it appears advisable to use pretreated eggshell for introducing CaO and MgO into a pigment, since the content of these oxides in eggshell is approximately 95 and 5%, respectively, while other ingredients are nearly totally absent.

The purity of this material should ensure the purity of glaze tinting, which has been confirmed experimentally. Thus, the idea of rational utilization of natural resources has become the basis for the study of the application of eggshell in the ceramic industry.

We chose chicken and ostrich eggshell as initial materials. Their spectral analysis reveals a nearly complete absence of colorant elements, except for some traces of Fe, Cu, Mn in ostrich eggshell, which was found to impart special properties to pigments based on this eggshell.

The author has attempted to produce ceramic pigments based on eggshell for tinting a glaze developed by us (USSR Inventor’s Certif. No. 1122634) that is used to decorate majolica produced from color-burning clays and for high-temperature underglaze painting. The batch composition of the pigments is listed in Table 1.

The introduction of SnO_2 and $K_2Cr_2O_7$ as chromophores has led to the production of the “pink purple” pigment (USSR Inventor’s Certif. No. 1201244), as well as pigments of the following shades: pinkish-violet, ink, and lilac. Similar pigments shades are obtained from a stannic acid gel tinted by finely dispersed metallic gold particles in the presence of silver. The elimination of these expensive elements from the pigment composition decreases its production cost. When the components of eggshell powder are introduced in the form of oxides taken in the initial ratio, it is impossible to obtain pigments of the same tints, which proves the effect of the natural structure of the initial material on the coloring properties of the chromophores [7]. The application of ostrich eggshell produces a special variation of the color tone different from the pigment based on chicken eggshell, while the main coloring is preserved. This is presumably due to the presence of small quantities of Fe and Cu in ostrich eggshell.

The phase composition of pigments depends on the composition of its oxide components. For instance, the gray pigment contains mainly simple and complex calcium-bearing silicates, and the pink pigment contains stannate or Sn-perovskite (Fig. 1). The pseudocubism of perovskite together with numerous laminar formations suggests that in the case of an equimolar replacement of TiO_2 by SnO_2, the chromophore ions may continue their incorporation into the lattice at the sintering temperature, provided there are auxochromes and mineralizing agents. The ions of Cr^{3+} that are partly incorporated into the SnO_2 lattice impart the “pink purple” shade to this pigment [5, 8].

TABLE 1

Material	Content, %, in mixture			
	1	2	3	4
Eggshell:				
chicken	31	30	–	–
ostrich	–	–	31	30
Perlite	10	50	10	50
Borax	10	–	10	–
Boric acid	–	10	–	10
SnO_2	45	–	45	–
$K_2Cr_2O_7$	4	–	4	–
Co_2O_3	–	5	–	5
Cr_2O_3	–	5	–	5

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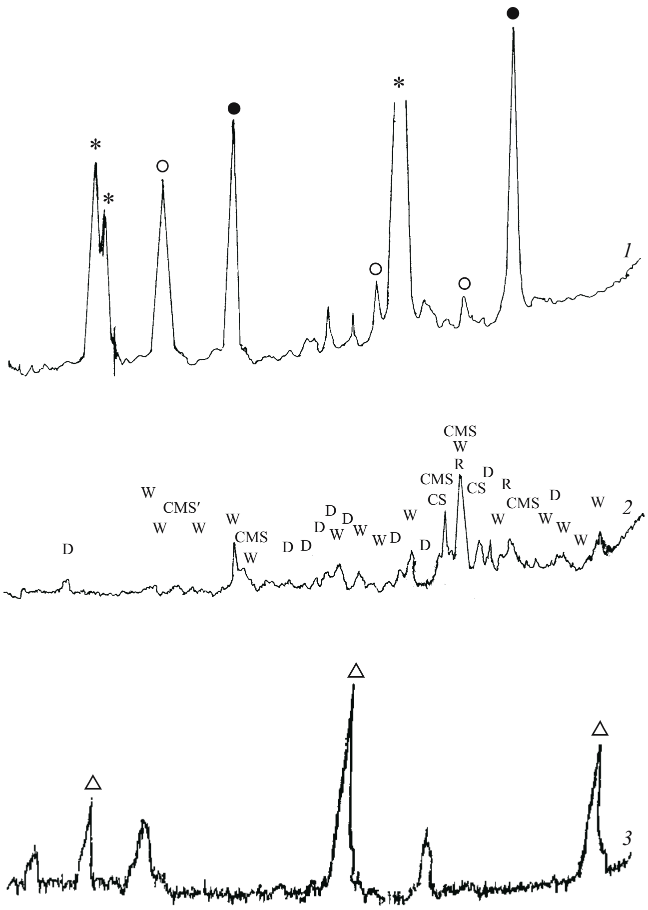

Fig. 1. X-ray diffraction patterns of pink (*1*) and gray (*2*) pigments and eggshell powder (*3*): ●) $CaSnO_3$; ○) SnO_2; ∗) borates; R) $Ca_3Si_2O_7$; W) $CaSiO_3$; CS) Ca_3SiO_5; CMS) $CaO \cdot MgO \cdot SiO_2$; CMS′) $Ca_2MgSi_2O_7$; D) $CaMg(SiO_3)_2$; △) $Ca(OH)_2$.

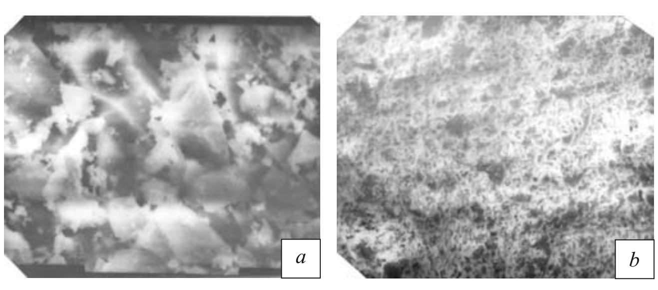

Fig. 2. Electron microscope photos (× 10,000) of pink (*a*) and gray (*b*) pigment powders.

The x-ray diffraction patterns[2] show some lines that are hard to identify unambiguously. However, it can be assumed that, apart from the above specified compounds, borate compounds may be formed as well. The absence of silicate in the pink pigment contradicts its oxide composition, but considering that SiO_2 is introduced into the pigment mixture via natural glass (perlite) in an amount not more than 10%, this may account for the absence of reflections that are typical of silicates.

[2] I am indebted to I. V. Pishch, Professor at the Department of Glass and Ceramic Technology of the Belarus State University, for his assistance in x-ray diffraction analysis.

TABLE 2

Glaze	Color coordinates			Chromaticity coordinates	
	X	*Y*	*Z*	*x*	*y*
Pink-lilac	58.14	56.51	62.96	0.327	0.318
Gray	70.13	71.47	76.69	0.321	0.327

Let us consider in more detail cobalt and chromium ions that are first-order chromophores. Introducing their oxides in equal quantities yields the best results. Apart from the green color that was expected (in the context of the contemporary theory of electron configuration of transition elements), we have obtained the following shades: grayish, light ashen, agate, greenish-ashen, and grayish-white.

Analogs of theses pigments are very rare. They are synthesized using expensive platinum and iridium oxides. The $[CoO_4]^-$ tetrahedron, which is an intense chromophore, is well studied and all possible maxima in its absorption spectrum are represented. The rare gray color with different shades that has been obtained in our case can be produced only with a particular ratio of cobalt and chromium, assuming that the elements introduced with eggshell have a polarization effect on them. As a consequence, we observe a deformation of the vacant *d*-shell of the transition elements, which has a perceptible effect on the transmission — reflection process and, accordingly, influences the type of tinting.

All diffraction maxima exhibit an insignificant deviation from certain interplanar distances, which indicates the formation of complex structural complexes or solid solutions in sintering. This is due to the fact that CoO is replaced by the chromophore oxides, which leads to the formation of an original tint spectrum. The content of perlite in this pigment reaches 50%. The microphotos (Fig. 2) may serve as the confirmation of the above. It should be noted that the powder crystals show a specific morphology of aggregate particles, and we can observe their different sizes, peculiar cutting, sometimes rounded forms with a "friezed" surface. Irregular-shaped facets have uneven edges and occasionally resemble argillaceous particles; porosity is absent.

Table 2 gives color characteristics calculated by the method of selected ordinates based on 10 points for the color source C.

The obtained ceramic pigments are produced according to a simplified production technology, have high heat resistance, original tints, a low production cost, and surpass the pigments currently used in the ceramic industry.

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